JOURNAL OF MATERIALS SCIENCE **33** (1998) 4887 – 4892

Development of glass frit free metallization systems for AlN

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Currently only glass bonding thick film conductor systems are commercially available for metallizing AlN-ceramic. The glass phase formed between metallization and ceramic impairs the high thermal conductivity of AlN. A new glass frit free metallization system has been developed utilizing the bonding mechanism of active brazing to provide the adhesion of metallization onto the ceramic. Aspects of paste preparation range from the derivation of the metallic powder to the selection of an appropriate printing vehicle which must decompose completely during the firing process under an inert atmosphere. The adhesion strength of the new paste system with the alternative bonding mechanism has been evaluated and contrasted with that of standard thick film pastes. © *1998 Kluwer Academic Publishers*

1. Introduction

Because of its high thermal conductivity aluminium nitride has been proved as a very competitive substrate material for power electronics applications. A range of standard thick film pastes are available for the metallization of ceramics. Glass frits or different oxides which are added to thick film conductor pastes are responsible for the adhesion of metal film on conventional alumina substrates. Unfortunately, only glass frit containing pastes are suitable for applications onto AlN–ceramic substrates. The advantage of high thermal conductivity will be affected by the glass phase acting as interlocking layer. Up until now no chemical bonding thick film conductor system for AlN has been available which would provide an interface of low thermal resistance. In the course of ongoing research regarding the nature of the thermal barrier occurring at the ceramic/metal interface, AlN ceramics had to be metallized using screen printing technology. With the goal of finding metallization systems resulting in smaller thermal resistance, a glass frit free thick film paste was developed.

A suitable screen printing ink must meet following requirements:

1. It must be printable. Therefore, the viscosity η under shear must be below a critical value.
2. The printed and fired metallic layer must be sufficiently thick to provide high electrical conductivity. Therefore, the solid particle content of the paste should be as high as possible.
3. The printed pattern must not bleed in order to achieve high resolution. This requires a high yield stress σ_0 and an average particle size below 3 μm.
4. The adhesion of the as printed layer onto the ceramic must be sufficient to allow handling further processing.
5. After firing the printed layer must be well bonded to the substrate in order to assure device integrity and reliability.

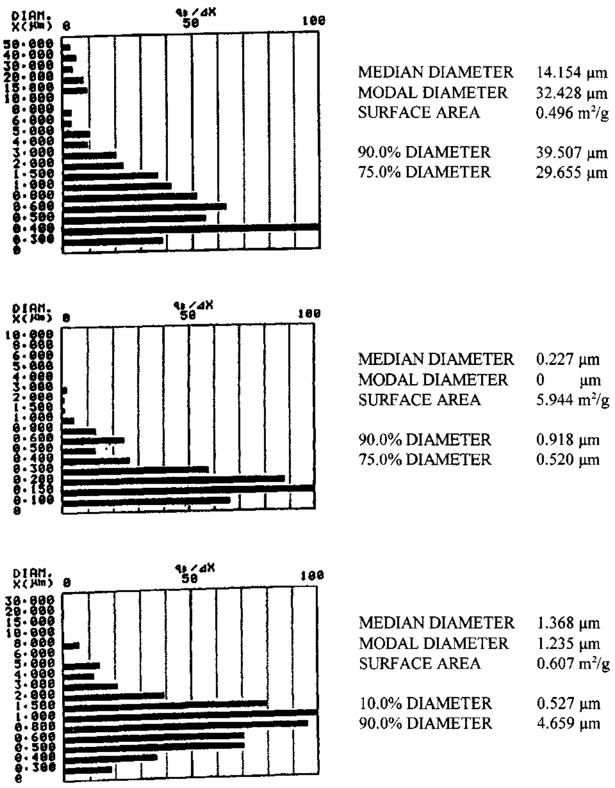
To meet these requirements thick film pastes are synthesized from solid state metallic powder(s) having particle sizes $\leq 3\,\mu$m and suitably chosen alloy compositions, as well as an organic carrier consisting of a polymer in a suitable solvent, a plasticizer, and a wetting agent.

2. Synthesis of the metallic powder

In glass free thick film metallization systems the metallic phase itself must bond to the substrate ceramic after firing. Using the CuAg eutectic as the base alloy for AlN metallization, addition of Ti (or Zr, or Hf) results in an interfacial reaction yielding TiN and $\eta Ti_3Cu_2AlN_{0.7}$ as bonding phases [1, 2, 3]. To be suitable for screen printing applications the alloy must be prepared as powders having $\leq 3\,\mu$m particle size.

Ti doped (up to 5 at %) CuAg eutectic alloy having such particle size as well as narrow size distribution were obtained as follows:

The intermetallic compound Ti_2Cu_3 was synthesized from Ti (purity: 5 N) and Cu (purity: 4 N) ingots (both from Johnson Matthey GmbH Alfa Products, Karlsruhe, FRG) by arc melting under pure argon followed by heat treatment for alloy embrittlement (sealed in evacuated quartz tubes at 800 °C for 600×10^3 s). After water quenching the 2 g button was crushed and wet milled in several runs under ca. 5 ml diethylene glycol



MEDIAN DIAMETER	14.154 µm
MODAL DIAMETER	32.428 µm
SURFACE AREA	0.496 m²/g
90.0% DIAMETER	39.507 µm
75.0% DIAMETER	29.655 µm

MEDIAN DIAMETER	0.227 µm
MODAL DIAMETER	0 µm
SURFACE AREA	5.944 m²/g
90.0% DIAMETER	0.918 µm
75.0% DIAMETER	0.520 µm

MEDIAN DIAMETER	1.368 µm
MODAL DIAMETER	1.235 µm
SURFACE AREA	0.607 m²/g
10.0% DIAMETER	0.527 µm
90.0% DIAMETER	4.659 µm

Figure 1 Particle size distribution analysis for Ti_2Cu_3-powder: (a) after wet milling; (b) after centrifugation and for $Ag_{0.6}Cu_{0.4}Ti_x$; (c) derived by polyol process.

(DEG) in a WC-mortar (type MS from Verder-Retsch GmbH, Haan, FRG). Mean particle size as well as size distribution was controlled after each milling run using a centrifugal particle size analyser (Model SACP-4 from Shimadzu, Kyoto, Japan). Upon reaching the milling limit (i.e. no significant size reduction from one milling step to the next) the powder had a mean particle size of $\geq 10\,\mu$m and a broad particle size distribution (Fig. 1a). This powder was ultrasonically suspended in 120 ml DEG and the coarse particle fraction was separated by centrifugation (3000 r.p.m., 4 °C, 240 s). The remaining suspension contained Ti_2Cu_3 powder having a mean particle size below 0.2 μm (Fig. 1b). To suitably selected aliquots of this suspension additional DEG as well as Cu(II)acetate (purum; from Sigma-Aldrich GmbH, Wien, Austria) was added and heated under reflux in order to reduce the salt to the metal in a so called "polyol process" [4]. Upon precipitation of the "intermediate phase" (IP) Ag(I)acetate (purum; from Sigma-Aldrich GmbH, Wien, Austria) suspended in DEG was added dropwise. The total metal content was 0.1 mole per 250 ml DEG. The reaction was allowed to continue until a clear solution above a metallic sponge occurred. The $Ti_xCu_{0.4}Ag_{0.6}$ powder obtained after hot filtration, washing and drying (at 60 °C) had a mean particle size $< 2\,\mu$m (Fig. 1c) and thus was suitable for screen printing ink preparations.

3. Selection of the organic vehicle components

The organic components of a screen printing ink provide the processing properties necessary during the printing stage, but must be removed during initial period of firing stage. Because Cu which is part of a paste composition is not stable upon heating in an oxidizing atmosphere and firing must done under inert or reducing conditions, a high molecular weight polymer (controlling the ink viscosity for keeping the metal powder(s) dispersed and providing the required thixotropy) was selected, which decomposes completely into gaseous species in non-oxidizing atmosphere: polyacrylic acid (PAA) with a molecular weight (M) from 50 000 to 100 000 (obtained from Fluka AG, Buchs, Switzerland). This polymer was found insoluble in either of the most common screen printing ink solvents α-terpineol or t-butanol. However, Hildebrandt parameters (δ) of PAA are listed [5] and range from 19.4 to 29.7 $\mathrm{MPa}^{1/2}$ in liquids having a strong tendency to form hydrogen bonds, and range from 18.2 to 22.1 $\mathrm{MPa}^{1/2}$ in liquids with medium tendency to form hydrogen bonds. This was used as guide to select liquids to be screened as solvents for PAA. The solubility of PAA was tested in mass ratios 1 : 10 (2 g PAA in 20 g solvent) and 1 : 15 (1.33 g PAA in 20 g solvent) at room temperature and at 50 °C (the temperature limit for PAA stability is 60 °C). The results are shown in Table I. The polymer solutions obtained were characterized with regard to the thixotropy coefficient (ζ_T) using a rheometer (Model Rheolab, from Paar-Physica, Stuttgart, FRG). The thus "predissolved" PAA could be brought into α-terpineol and be dissolved therein.

The main additives to improve the rheology of the ink are plasticizer and surfactant. The plasticizer is thought to reduce the stiffness of the polymer by modifying the wetting between the polymer and the solvent. Thus the coefficient B of the van't Hoff equation for the osmotic pressure Π

$$\Pi = RTc/M + Bc^2 \qquad (1)$$

(where R is the gas constant, T the temperature and c the concentration) was used as a criterion to identify potential plasticizers, because B depends on the interaction between polymer and solvent and thus characterizes the solvent with regard to the polymer [6]. Because of lack of comprehensive data compilations for B, values were estimated from data for the Hildebrandt parameter [5] using

$$B \sim \frac{1}{2\pi}\left(\delta_D - \left(\frac{2}{3}\right)^{1/2}\delta_P\right) \qquad (2)$$

TABLE I Solubility behaviour of PAA in various solvents

Solvent:	δ (MPa)$^{1/2}$	Solubility of PAA	ζ_T
α-terpineol	18	Unsoluble	
t-butanol	21.7	Unsoluble	
PEG 200	26.3	Dissolved at RT after 24 h; at 50 °C after 24 h	7.00
Ethanol	26.6	Dissolved at RT after 24 h; at 50 °C after 1 h	1.48
Methanol	29.7	Starts to swell at RT after a certain time	
DEG	29.9	Dissolved at RT after 24 h; at 50 °C after 2.5 h	5.84
Ethyleneglycol	32.9	Unsoluble	

where δ_D is the dispersive term of the Hildebrandt parameter and δ_P is the polar term of the Hildebrandt parameter.

All readily available liquids, which had a high calculated B value, were tested for suitability as plasticizers by a simple solubility and "painting" test. Dibutylphatalate (DBP) is soluble, does not precipitate PAA from the solution, produces a shiny surface upon painting the mixture, and was thus selected as plasticizer.

Surfactants are additives, which should reduce the interfacial tension between the organic vehicle and the metal particles. Literature repeatedly mentions the usefulness of surfactants [7, 8], but does not mention specific substances. Starting from the consideration, that interfacial tension reducing agents should have themselves a low surface tension, literature data on the surface tension of liquids [9] were screened. Of the liquids with the lowest values listed, isopentane, n-hexane, and t-butanol, only the last was soluble in α-terpineol and thus was selected.

4. Preparation of the screen printing ink

The higher the content of the solid phase in the ink, the better is the density and homogeneity of the screen printed pattern. On the other hand, dispersion of fine solid particles in a liquid phase increases the viscosity η exponentially with the fraction of solid [10]. To assure printability the viscosity must be ≤ 60 Pa s limiting thus the maximum fraction of solid phase acceptable in the ink. Fig. 2 shows viscosity versus metal content in a solution of 1.2 mass % PAA in α-terpineol. Within the coordinates metal powder/polymer-solvent the highest metal powder content of 63 mass % was observed for solutions containing between 0.4 and 1.9 mass % PAA. The addition of DBP as plastisizer and t-butanol as surfactant permitted to increase the solid phase fraction close to 70 mass %. Table II gives two optimized "standard" ink compositions resulting from these series of experiments. The two last mentioned components are essential for the quality of the ink. It was found, that the ratios between DBP and α-terpineol, between DBP and the metal powder, and between t-butanol and the 1 : 10 PAA in DEG polymer solution should be kept constant.

TABLE II Standard ink compositions

Component:	Ink #1 (Wt %)	Ink #2 (Wt %)
PAA:DEG (1:10)	13.1	7.3
α-terpineol	12.9	14.5
Metal powder	60.7	67.9
DBP	5.4	5.9
t-butanol	7.9	4.4

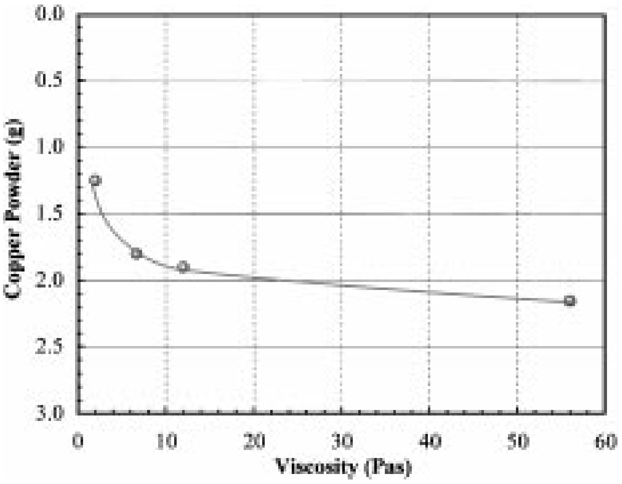


Figure 2 Change of viscosity η with increasing metal powder content in the ink (polyol derived Cu, mean particle size 2.36 μm; dispersed in solution of 1.2 mass % PAA in α-terpineol).

5. Performance of metallization

5.1. Experimental/Preparation of metallization pads

Besides the printability of the paste formulation the adhesion of the resulting metallization onto the AlN-ceramic is a significant criterion which must be considered with regard to evaluate the suitability of the glass frit free AgCuTi-metallization system as an alternative to the conventional glass bonded thick film pastes. The adhesion strength of metallizations is usually determined by means of the so called nailhead test. For this purpose nail-head pins are bonded to the surface of metallization pads whose bonding strength should be analysed. A pulling force is applied on the pins and continuously increased until failure occurs. Provided that the metallization is lifted off, the measured force can be assigned to the adhesion strength of the metallization.

In order to realize the metallization pads required for adhesion testing the ink composition #1 (Table II) has been selected for this application. The considered paste was applied onto AlN-substrates by a conventional screen printing process utilizing a 200 mesh stainless steel screen coated with a 30 μm thick capillar film stencil (Murakami, Japan). In order to achieve a voidfree continous metallization the paste was applied in three layers. Each layer was dried and fired seperately. The total thickness of fired metallization varied between 80 and 100 μm. The extraordinary layer thickness provides to determine either the adhesion of the metallization onto the ceramic or the cohesion within the metallization.

After printing the paste layers were initially levelled at room temperature for few minutes and dried at 75 °C for 10 min in a drying furnace. Firing the samples has been carried out in a conventional thick film furnace under an argon atmosphere with a maximum oxygen content of 15 vol p.p.m. at a peak temperature of 850 °C. In comparison to the standard heat profile of the conventional thick film process the total cycle time has been increased from 60 min to 180 min and in consequence also the dwell time at peak temperature from 10 min to 30 min.

5.2. Bonding strength

The pull tests have been conducted with metallizations realized by our experimental glass frit free

AgCuTi-conductor composition, as well as by commercially available glass frit containing copper pastes for comparison purpose. In contrary to our glass frit free conductor paste the copper pastes were fired at the standard thick film heat profile under nitrogen atmosphere (dwell time at peak temperature: 10 min, total cycle time: 60 min). Epoxy precoated aluminium nail head pins were bonded on the surface of the metallization pads. The test samples were inserted in a pull tester and the pulling force at bonding failure determined.

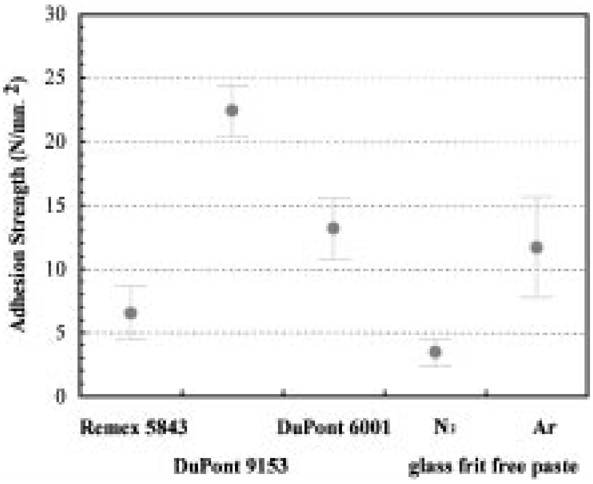
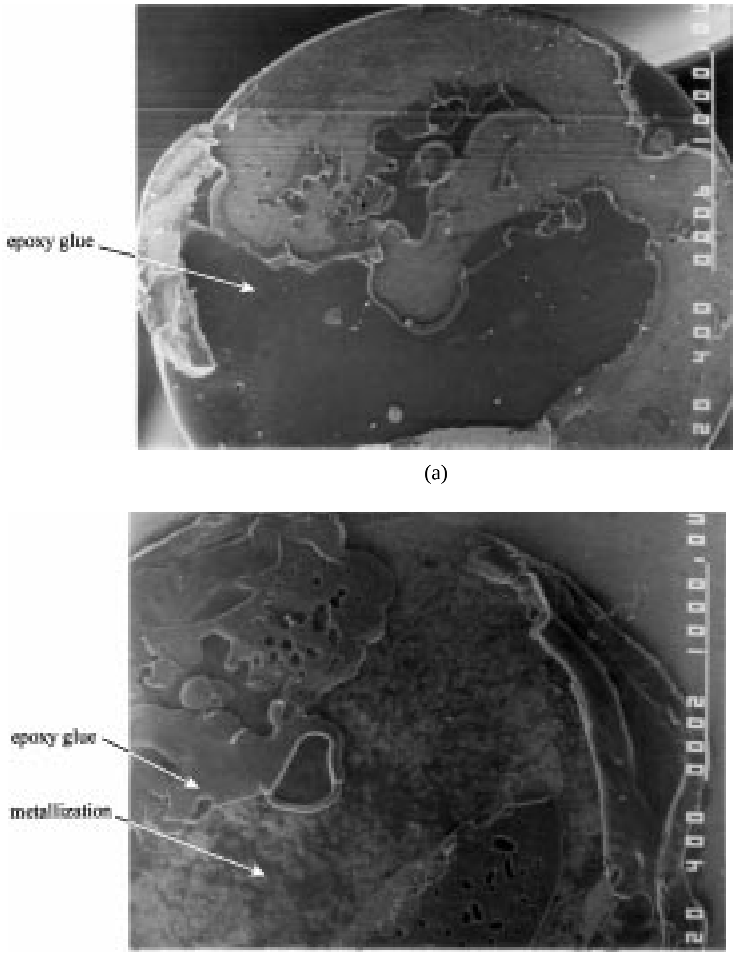


Figure 3 Adhesion strength commercially available glass frit containing copper pastes and experimental glass frit free AgCuTi-paste (containing 2.5 at % Ti, firing temperature 850 °C, dwell time 30 min) fired under nitrogen as well as under argon.

The pull test yields an adhesion strength of the AgCuTi-metallization which is comparable to that of different glass bonded copper pastes (Fig. 3). The excellent adhesion of metallization is also documented by scanning electron microscope (SEM) photographs (Fig. 4) of the lifted-off nail heads and the corresponding area of the metallized AlN-substrate where the studs have been attached. The metallization could not be removed from the substrate by the applied force. It must be supposed that the adhesion strength of the metallization is quite higher as recorded in the graph of Fig. 3. Actually, the tensile strength might be limited by the bonding strength of the epoxy glue. This fact may be related to irregularities of the surface profile of the metallization which impedes an uniform glue wetting of the pads.

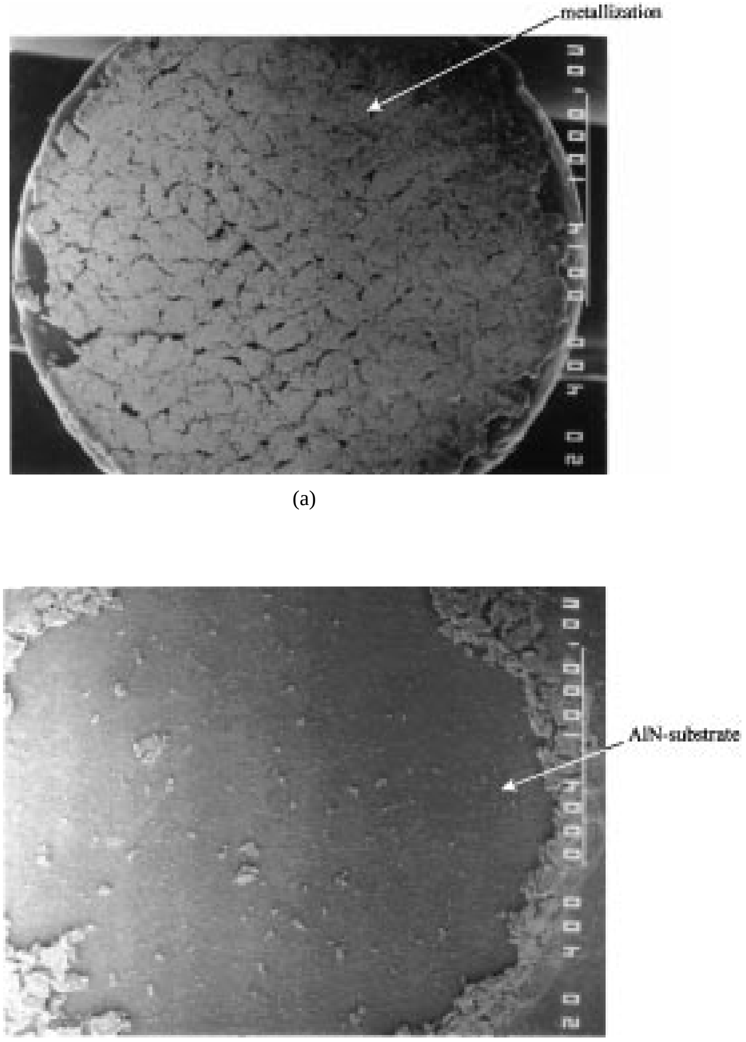
The high adhesion strength must be related to the development of Ti enriched layers at the interface between metallization and ceramic. The structure and the morphology of the interface comprising such interlocking Ti enriched layers between AgCu metallization



(a)

(b)

Figure 4 SEM micropraph of (a) nail head and (b) corresponding AlN-substrate area after exposure to pull test (paste containing 2.5 at % Ti, firing temperature 850 °C, dwell time 30 min, firing atmosphere argon).



(a)

(b)

Figure 5 SEM micropraph of (a) nail head and (b) corresponding AlN-substrate area after exposure to pull test (paste containing 2.5 at % Ti, firing temperature 850 °C, dwell time 30 min, firing atmosphere nitrogen).

and aluminium nitride ceramic have been detected in a transmission electron microscope (TEM) by Carim and Loehman [1] who studied the reactive bonding mechanism of titanium doped metal foils and aluminium nitride. Based on this study it can be assumed that such Ti rich layers must have been already formed, although in a SEM–energy dispersive X-ray (EDX) analysis we could not detect any Ti enrichment at the interface. It must be supposed, that these interfacial reaction product layers were too thin ($< 2\,\mu$m) to be identified by SEM–EDX.

For comparison purpose the screen printed AgCuTi paste has been fired also under nitrogen atmosphere. The pull test carried out with these samples results only in a poor adhesion strength of the metallization, which is also reflected in the compiled data of the graph in Fig. 3, as well as documented in the SEM photographs of Fig. 5. Evidently under the nitrogen atmosphere the dispersed Ti particles react already with the surrounding atmosphere and TiN is formed. Consequently the driving force for the Ti diffusion towards the interface between metallization and the ceramic, responsible for adhesion strength, is lost.

6. Conclusion

The development of the glass frit free thick film metallization system depends on the activation of an alternative bonding mechanism between the metallization and the ceramic. The bonding mechanism which is based on an active brazing process operates only if paste firing is conducted in another inert atmosphere but in nitrogen. The results of the pull test have shown an adhesion strength of metallization comparable with that achieved with glass fritted standard thick film pastes. The electrical characteristic as well as solderability of metallization will be further topics of investigations.

Acknowledgement

The authors are very indebted to the Fonds zur Förderung der wissenschaftlichen Forschung for the financial support of this project (Project: P 10304-PHY).

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Received 10 March
and accepted 18 June 1998